

Giant magnetoresistance for ensembles of ferromagnetic granules in variable range hopping conductivity regime

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Abstract

We study an effect of moderate magnetic field on variable range hopping conductivity in arrays of ferromagnetic granules separated by tunnel barriers. It is shown that the resulting magnetoresistance can be significantly larger than the standard "giant" magnetoresistance in Fe-N-Fe-N... multilayers. The effect is related to a gain in densities of states available for the virtual processes within the intermediate granules due to magnetic-field induced alignment of the granule magnetizations.

I. INTRODUCTION

During last decades a significant interest was paid to transport properties of metallic nanostructures which are considered as key elements for different technologies including new nanoelectronic devices (see, e.g., [1]). Important example of such nanostructures is related to composites of metallic nanogranules separated by dielectric (oxide) barriers. According to an extended set of experimental data, the low-temperature conductance of such structures exhibits the Efros-Shklovskii law $\sigma \propto \exp -(T_0/T)^{1/2}$ typical for variable range hopping conductivity [2]. The typical explanation for such a behavior was assumed to be a correlation between sizes of the metallic granules and of the intergranular distances [3].

Surprisingly, only several years ago a mechanism directly relating the temperature behavior in question to the variable range hopping (VRH) was suggested [4],[5] [6] . An important feature of this mechanism was an assumption that the transport was controlled by hops between remote granules. The choice of corresponding pair of granules corresponds to optimization of the sum of intergranular tunneling action and activation exponent related to a random potential of the structure (which is typical for VRH). However, in contrast to the standard VRH([2]), the "hopping trajectory" in this case inevitably includes some "intermediate" granules which play a role of "under-barrier scatterers" like in theory of interference-mediated VRH [7]. Another important ingredient of this mechanism was so-called co-tunneling, which included both an "elastic" channel when the transport was supported by the single intermediate states within the intermediate granules, and "inelastic" channel when the transport was supported by two different electron states within at least some of the intermediate granules ([6]).

An important progress achieved in last years was related to a possibility to fabricate aggregates of nearly monodisperse nanogranular structures [8] . This progress allowed to exclude the mechanism of ([3]), concentrating on the mechanism of hopping including "intermediate" granules. In addition, the technique exploited in ([8]) allowed to obtain aggregates of ferromagnetic granules (in particular, on the base of Ni, [5]). One notices, that in the case of ferromagnetic granules one expects an important effect of the spin correlations for the hops including granules with different orientations of magnetization. In particular, one expects that a presence of external magnetic field leading to an alignment of magnetizations in different granules can significantly affect the hopping transport which results in pronounced

magnetoresistance. Note that the effect of negative magnetoresistance in ferromagnetic nanostructures was extensively discussed starting from well-known, effect of so-called giant magnetoresistance (GMR) (see, e.g., [9]) appeared to be extremely useful for applications. The simplest example of its experimental realization is related to multilayers Fe-N-Fe... where Fe stands for a ferromagnetic layer while N stands for a normal metal layer. When the magnetizations of all Fe layers are aligned (which, in particular, can be controlled by a relatively weak external magnetic field) an electron with a given spin direction stays to belong to the same group of minority or majority electrons in all Fe layers provided the spin relaxation length is large enough. While the partial contributions of the minority and majority groups in Fe layers are different, it can be proved that the alignment mentioned above leads to a decrease of total sample resistance with respect, to say, to random orientation of different Fe layers. Among latest studies in this direction we can mention, in particular, the papers [10] [11], [12]. However, the attention was mainly paid to tunneling transport involving two neighboring ferromagnetic layers or granules. In what follows we will concentrate on variable range hopping through ensembles of ferromagnetic granules involving co-tunneling. An important factor leading to an enhancement of the magnetoresistance in this case is related to the fact that each hop involves many intermediate granules. Thus, the alignment of magnetizations within the intermediate granules leads to multiplication of the effect expected for tunneling between two neighboring granules.

The system in question is an ensemble of ferromagnetic granules with tunnel barriers between the granules, which implies that the charge transport through the system is due to hopping. The thin films formed by granules of different metals with typical size 2-5 nm were obtained in our institute several years ago with a help of laser electrodispersion (see e.g. [8]). The thickness of the film started from monogranular layers while the character and magnitude of the conductivity were dependent both on film thickness and technological factors. At least, the Ni-based structures which clearly demonstrated Efros- Shklovskii variable range hopping were also fabricated.

First, we will give a short discussion of hopping between granules from normal metal, based mostly on the results of [6], then will consider the consequences for ferromagnetic granules. Note that the problem of variable range hopping in ensembles of ferromagnetic granules imply many-particle effects related to different granules. Thus to attack this problem it was necessary to restrict ourselves by the minimal model concerning the intergranular

tunneling. In particular, we will not go into details related to band structure of the ferromagnetic materials except of a presence of minority and majority carriers.

II. VARIABLE-RANGE CO-TUNNELING IN ENSEMBLES OF NORMAL METAL GRAINS

An important factor responsible for the variable-range hopping in granular structures is related to the fact that such a hopping inevitably involves for each hop between the remote granules a supporting role of virtual electron states in intermediate granules (see, e.g., [4, 5]). Indeed, in contrast to standard hopping conductivity via impurity states in semiconductors, here there is no "direct" tunneling path - the shortest line connecting any two granules except the neighboring ones inevitably crosses some intermediate granules. In other words, hopping in this case implies so-called co-tunneling (elastic or inelastic - see, e.g., [6]).

For demonstration, we will consider 3-granule array implying a hop between granules 1 and 3 through the granule 2. Elastic co-tunneling implies a presence of a single intermediate virtual state. For elastic co-tunneling an electron, starting from the initial granule 1 (virtually) occupies one of the states within the intermediate granule (2) and then occupies the final state within the granule 3. For the case of inelastic co-tunneling an electron starting from granule 1 virtually occupies *one* of the available states within granule 2 while *another* electron starting from *another* state within the granule 2 finally occupies the final state within the granule 3.

The important detail of such a co-tunneling (and of VRH conductivity in granular materials) is related to the following. As it can be easily estimated, for a granule with a radius of the order of several nm the charging energy can reach $10^{-13} \text{erg} \sim 10^3 K$. So, at low temperature most of the granules are Coulomb blockaded. However the effect of the Coulomb blockade can be partially lifted due to disorder potential related, say, to traps within the insulating barriers. Due to this disorder there is a small number of granules with relatively small energy of Coulomb blockade estimated with respect to "global" chemical potential over the sample. The hopping is possible only between these rare granules. However to reach the distant granule with small Coulomb blockade energy the electron should pass through virtual states (co-tunnel) on intermediate granules.

The most general expression for the tunneling amplitude between two distant granules

including both elastic and inelastic co-tunneling can be found in [6]. In our work we adopt several simplifications that do not interfere with discussed physics and allow us to make the expressions significantly simpler. First, we consider only inelastic co-tunneling. Second we consider Coulomb blockade energies on intermediate granules to be much larger than Coulomb blockade energies of starting and final granules of the hop. Third, we neglect the changes in the Coulomb gap energies of intermediate granules due to position of tunneling electron. Finally, we neglect the difference between different "time orderings" discussed in [6]. These assumptions allow us to ascribe some fixed Coulomb blockade energy to each intermediate granule. We will show that this approach allows us to catch the qualitative results of [6] and discuss the novel phenomena appearing due to the ferromagnetic nature of granules.

Inelastic hopping process includes two states within each of the intermediate granules k : the electron state e_k is the state to which the electron tunnels from the previous granule $k - 1$, and the hole state h_k from which the electron tunnels to the next granule. Let us write the contribution to the tunneling probability from a given ensemble of states $\{e_k, h_k\}$

$$P\{e_k, h_k\} \propto \frac{\prod_{k=0}^N f(h_k) t_{h_k, e_{k+1}}^2 (1 - f(e_{k+1}))}{\prod_{k=1}^N E_{C,k}^2} \delta\{e_k, h_k\}. \quad (1)$$

Here we consider N intermediate granules $1...N$. The index $k = 0$ stands for the initial granule of the hop and the index $k = N + 1$ is for the final granule of the hop. $t_{h_k, e_{k+1}}$ is the tunneling matrix element between states h_k and e_{k+1} . f is the fermi function and $E_{C,k}$ is the Coulomb gap energy of k -th granule. $\delta\{e_k, h_k\}$ — is the delta function from the total energy determined by all the ensemble of states. It ensures energy conservation during the hop.

To get the full tunneling probability P one should sum $P\{e_k, h_k\}$ over all possible ensembles of states

$$P = \sum_{\{e_k, h_k\}} P\{e_k, h_k\}. \quad (2)$$

Without the effects of ferromagnetism, this summation yields

$$P \sim \frac{t^{2N} g^{2N} \epsilon_{inel}^{2N}}{E_C^{2N}} \exp \frac{-\epsilon_{0,N+1}}{T}. \quad (3)$$

Here t is the characteristic value of tunneling matrix element between adjusted granules, E_C is the characteristic value of Coulomb gap energy, g is the density of states near the Fermi

level in a single granule, T is the temperature, $\epsilon_{0,N+1}$ is the absolute value of the difference of electron energies on initial and final granules and $\epsilon_{inel} \sim \epsilon_{0,N+1}/N$ is the characteristic inelastic energy. Note that expression (3) agrees with the results of [6] for inelastic co-tunneling.

III. EFFECT OF FERROMAGNETISM

Let us now include in our consideration the ferromagnetic ordering inside granules leading to a presence of magnetization within each granule. We will assume that the overlapping integrals between different neighboring granules are small enough (which is natural for systems with hopping conductivity) and thus the intergranule exchange interaction can be neglected. At the same time different granules are expected to have different orientations of the anisotropy axes and thus magnetization orientations $\mathbf{n}_{J,k}$ for different granules are different. Then, in each granule we have different densities of states for majority (g_M) and minority (g_m) electrons. It can be shown that the square of the tunneling amplitude between two majority states or two minority states in the adjacent granules is proportional to $(1 + \cos \theta_{k,k+1})/2$, where $\cos \theta_{k,k+1} = \mathbf{n}_{J,k} \cdot \mathbf{n}_{J,k+1}$. The majority→minority and minority→majority tunneling amplitude squares are proportional to $(1 - \cos \theta_{k,k+1})/2$. Thus the contribution of tunneling probability $P\{e_k, h_k\}$ acquires additional factors corresponding to these cosines

$$P\{e_k, h_k\} = P\{e_k, h_k\}^{(0)} \cdot \prod_{k=0}^N \mathcal{C}_{k,k+1}, \quad (4)$$

where $P\{e_k, h_k\}^{(0)}$ is determined by expression (1) with spin independent tunneling matrix elements $t_{k,t+1}$, $\mathcal{C}_{k,k+1}$ depends on the nature (minority or majority) of states k and $k+1$:

$$\mathcal{C}_{k,k+1} = \begin{cases} (1 + \cos \theta_{k,k+1})/2 & M \rightarrow M, m \rightarrow m, \\ (1 - \cos \theta_{k,k+1})/2 & m \rightarrow M, M \rightarrow m. \end{cases} \quad (5)$$

Here M stands for majority states and m for minority.

The difference between the majority and minority density of states should be taken into account in the summation procedure (2). For the ferromagnetic granules this procedure leads to the following result

$$P \sim P^{(0)} \prod_{k=0}^N (1 + \mathcal{P}^2 \cos \theta_{k,k+1}), \quad (6)$$

where $P^{(0)}$ is given by the expression (3) and $\mathcal{P} = (g_M - g_m)/(g_M + g_m)$ is the polarization inside granules.

We assume that the conductivity of the sample is proportional to averaged tunneling probability. So to calculate the magnetoresistance one should average (6) over angles $\theta_{k,k+1}$. Note that, strictly speaking, angles $\theta_{k,k+1}$ are not independent (although the directions $\mathbf{n}_{J,k}$ are independent). However we will proceed considering values of $\theta_{k,k+1}$ as independent. It can be shown that such an approach gives correct result for low fields (when Zeeman energy JH is much less than temperature) as well as for the saturation field (when $\theta_{k,k+1} \sim 1$). With this simplification we have

$$G(H)/G(0) = (1 + \mathcal{P}^2 \langle \cos \theta \rangle)^{\overline{N}+1},$$

where G is the system conductance, $\langle \cos \theta \rangle$ is the average value of the angle between magnetic moment of adjusted granules, \overline{N} is the characteristic number of intermediate granules. Note that for $\overline{N} = 0$ this result reproduces the result of [14] where intermediate granules were not included.

Now we will discuss the physics leading to the results obtained above. As for material parameters, we will base on the experiments [15] where nanocomposites of Ni granules with a granule size $\sim 2nm$ (containing about 600 atoms) were studied. The samples clearly demonstrated superparamagnetic behavior, however, for aggregates containing about 10^3 granules. The anisotropy constant K (entering to the estimate of anisotropy energy KV , where V is a granule volume) according to the experimental results can be estimated for a single granule as $\sim 10^6 erg/cm^3$. It was attributed to the shape anisotropy.

The physical picture naturally depends on the interplay between the Zeeman energy JH , the anisotropy energy KV and temperature T . When the anisotropy energy of the granules can be neglected with respect to the temperature or Zeeman energy (that is in relatively strong magnetic fields corresponding for the aggregates discussed above to fields larger than $\sim 0.1T$), it is possible to obtain the following expression for averaged cosines

$$\langle \cos \theta \rangle = m^2 = \left(\frac{1}{\tanh(JH/T)} - \frac{1}{JH/T} \right)^2. \quad (7)$$

Here m is the relative magnetization of the system and J is the magnetic moment of single granule.

At small fields expression (7) leads to quadratic magnetoresistance

$$\frac{\Delta R}{R} = -\mathcal{P}^2 \frac{\overline{N} + 1}{3} \left(\frac{JH}{T} \right)^2, \quad (8)$$

while at high fields $JH \gg T$ magnetoresistance saturates at the value

$$\frac{R(H)}{R} = (1 + \mathcal{P}^2)^{-\overline{N}-1}. \quad (9)$$

Note that expressions (8) and (9) are correct despite the approximation of independent $\theta_{k,k+1}$.

Let us also discuss another case when anisotropy energy is strong enough (and the Zeeman energy is relatively small), thus the magnetic moments are always oriented along the easy anisotropy axes. In this case it is important to know if the magnetic moments of the granules can flip between the directions along the easy axis. To change its direction the magnetic moment should overcome the barrier related to the anisotropy energy ($\sim KV$). This process occurs at the time scale $1/\tau \sim f_0 \exp(-KV/T)$ where f_0 is the attempt frequency. For realistic time scales of the experiment it is possible to introduce a blocking temperature $T_b \sim KV/25$ (see e.g. [15]). One notes that the granules can flip its magnetic momentum direction only when the temperature is larger than T_b (for details see [13])

Let us consider the situation of relatively strong anisotropy $KV > T$, JH , however still assuming that the temperature is larger than the blocking temperature T_b . (Note that basing on the results of [15] the blocking temperature for a single granule can be estimated as $< 1K$). So the magnetic moments can flip between the two possible directions along these axes minimizing the Zeeman energy. In general, we have a standard situation of the superparamagnetic particles. The relation $\langle \cos \theta \rangle = m^2$ holds in this case too, however the dependence of m on magnetic field is different (and more complex) than in the situation considered above. At small magnetic field we obtain for strong anisotropy

$$\frac{\Delta R}{R} = -\mathcal{P}^2 \frac{\overline{N} + 1}{9} \left(\frac{JH}{T} \right)^2, \quad (10)$$

and in saturation field within the approximation of independent angles

$$\frac{R(H)}{R} = (1 + \mathcal{P}^2/4)^{-\overline{N}-1}. \quad (11)$$

Thus in the case of strong anisotropy magnetoresistance has the same form and the same dependence on \overline{N} as in the case of weak anisotropy, but is somewhat weaker than in the case of weak anisotropy.

The relative strength of anisotropy in the system should be estimated with respect to the Zeeman energy as well as to the temperature. If the temperature is larger than anisotropy energy $T > KV$, we definitely have the case of weak anisotropy and the magnetoresistance should be described by equations (8) and (9). However at lower temperature $KV > T > T_b$ the strength of anisotropy should be compared to the Zeeman energy. At weak fields when Zeeman energy JH is still weaker than KV the magnetoresistance is controlled by equation (10) (for $JH < T$) and may even reach plateau given by eq. (11) for $JH > T$. However at stronger magnetic fields $JH \geq KV$ the effect of the anisotropy is suppressed by magnetic field. At this point the magnetoresistance goes up again and reaches its real saturation (described by eq. (9)) for $JH \gg KV$. Finally, when temperature is smaller than blocking temperature $T < T_b$ the magnetization is blocked if Zeeman energy is smaller than the anisotropy energy. At this case there is no magnetoresistance up to the fields $JH \sim KV$. At larger fields $JH \gg KV$ resistance saturates at the value (9).

According to our estimates, the effect crucially (exponentially) depends on the number of the intermediate granules N . Let us estimate the upper boundary for this number. The hopping character of the conductance implies that the intergranular conductance is much smaller than e^2/h . Having in mind the small size of the granules one expects that only small number of quantum channels in granules contribute to the conductance (this number is controlled by the cross-section of the tunneling area), we will assume that this number is at least less than 10. Thus the hopping character of the conductance implies that the tunneling transparency is much less than 0.1 which, in its turn, implies that the tunneling exponent is larger than 2. It gives the contribution of each intergranular contact to the total tunneling action corresponding to the hop. One has in mind that for the Coulomb gap hopping the total tunneling action gives to the hopping exponent ξ a contribution equal to $\xi/2$. Then, the largest measurable value of ξ is expected not to exceed 20. Thus the total number of the intermediate granules in this case is $10/2 - 1 = 4$. Since the exponents in Eqs.9,11 are equal to $N + 1$, in such a case one indeed expects a strong effect. Indeed, for polarization degree 1/2 the corresponding factor is equal to $(5/4)^5 \sim 3$. Certainly, this is rather an upper estimate of the predicted effect.

IV. CONCLUSIONS

To conclude, we have shown that the arrays of ferromagnetic granules separated by tunneling barriers can in variable range hopping regime exhibit giant magnetoresistance at least by order of magnitude exceeding the standard magnetoresistance in Fe-N-Fe... arrays. The origin of this magnetoresistance is related to the fact that for random directions of the granule magnetic moments the densities of states for the virtual processes within the intermediate granules participating in the hop are partly suppressed due to difference between systematics of minority and majority electrons within different granules. Then, the external magnetic field aligns the granule magnetic moments thus establishing a unique systematics of majority and minority electrons throughout the sample, thus increasing the corresponding densities of states. The large increase of the effect for variable range hopping conductivity is explained by a large number of the intermediate granules participating within a single hop event, the resulting magnetoresistance appears to be exponential in terms of this number.

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- [1] R.H.Chen, K.K.Likharev, Appl. Phys. Lett., **72**,61 (1998)
 - [2] B.I.Shklovskii, A.L.Efros, Electronic properties of doped semiconductors, Springer-Verlag, New York, 1984
 - [3] P.Sheng, B.Abeles, Y.Arie, Phys. Rev.letters., **31**, 44, 1973)
 - [4] J.Zhang, B.I.Shklovskii, Phys.Rev. B, **70**, 115317, 2004)
 - [5] V.I.Kozub, V.M.Kozhevin, D.A.Yasnin, S.A.Gurevich. Pis'ma v ZhETF, **81**, 287 (2005), JETP letters **81** 226 (2005)
 - [6] M.V.Feigelman, A.S.Ioselevich, Pis'ma v ZhETF **81** 341 (2005), JETP letters **81** 277 (2005)
 - [7] B.I.Shklovskii, B.Z.Spivak, Hopping transport in solids, eds. M.Pollak and B.Shklovskii, Elsevier, 1991
 - [8] V.M. Kozhevin, D.A. Yavsin, V.M. Kouznetsov, V.M. Busov, V.M. Mikushkin, S.Yu. Nikonov, S.A. Gurevich and A. Kolobov. JVST B, 18, 1402 (2000).

- [9] M.N. Baibich, J.M. Broto, A. Fert, F. Nguyen Van Dau, F. Petroff, P. Etienne, G. Creuzet, A. Friederich, and J. Chazelas, Phys. Rev. Lett. **61**, 2472 (1988).
- [10] W.H.Butler, X.-G.Chang, T.C.Schulthess, J.M.MacLaren, Phys. Rev. B, **63**, 054416 (2001)
- [11] N.Bonarjee,J.W.Robinson, A.Aziz, M.Ali, B.J.Hickey, M.G.Blamire, Phys. Rev. B, **86**, 134423 (2012)
- [12] X.-G.Zhang, Z.C.Wen, H.X.Wei, H.F.Han, Phys. Rev. B, **81**, 155122 (2010).
- [13] C.L.Dennis, R.P.Borges, L.D.Buda, U.Endes, J.F.Gregg, M.Hehn, E.Jouuelet, K.Ounadjjela, I.Peter, I.L.Prejbeam, M.J.Thornton, J.Phys.:Condens.Matter **14** (2002) R1175.
- [14] J. Inoue and S. Maekawa, Phys. Rev. B **53** R11927
- [15] Ilyushenkov D.S., Kozub V.I., Yavsin D.A.,Kozhevin V.M., Yassievich I.N., Thanh Trung Nguyen , Bruck E.H. , Gurevich S.A. Journal of Magnetism and Magnetic Materials **321**, 343 (2009)